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## MODELLING OF THE STRUCTURE AND STRUCTURAL TRANSFORMATIONS IN AMORPHOUS CHALCOGENIDES

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Computer relaxed structural models of arsenic based chalcogenide glasses allowed to demonstrate that the atomic configurations in these materials are anisotropic with a strong tendency to extend as disordered layers. In the frame of these models the photostructural transformations and photoinduced anisotropy find a straightforward explanation.

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### 1. Introduction

The atomic scale structure of non-crystalline chalcogenides is still a challenging problem. With the advent of surprising discoveries in the field of chalcogenide glasses, as e.g. the photoinduced anisotropy [1] and photoinduced fluidity [2] the problems related to the atomic scale structure and to structural modifications induced by light become more and more important.

In this paper are presented the main results obtained in the modelling of the structure of some arsenic based chalcogenides and of structural transformations in these glasses.

### 2. Modelling

The modelling of the non-crystalline arrangements of the atoms was carried out starting from simulated assemblies of atoms constructed by hand, with special building units. The coordinates of the atoms were measured by a cathetometer method and the tables of coordinates and atom bonding topology were introduced into computer. By using appropriate force constants for the covalent bonds between the atoms, after [3], and a Monte Carlo-Metropolis procedure for the minimization of the free energy of every model, we got a physically realistic structure. A FORTRAN computer program in Lynx system was run on a Pentium PC, in order to perform the energy relaxation of the atomic models.

### 3. Results

#### 3.1. Is there amorphous arsenic made of anisotropic layer-like configurations?

As stated by Krebs and Steffen [4] and by Breitling and Richter [5] the amorphous arsenic can be obtained in two forms:  $\beta$ -As and  $\gamma$ -As. Bulk samples and precipitated amorphous arsenic exhibit a  $\beta$ -type structure while evaporated films are of  $\gamma$ -type. The differences in the X-ray scattered intensities and the corresponding RFD's are evident in Fig. 1a,b.

The first sharp diffraction peak (FSDP) plays an essential role when the two forms are identified. Moss and Price [6] have shown that during annealing this peak increases and becomes narrow, thus suggesting a transition from  $\gamma$  to  $\beta$  form.

In order to explain the amorphous structure of arsenic, firstly microcrystalline models were tried. Two types of As-crystal do exist: a rhombohedral phase (Rh-As) and an orthorhombic (Or-As) one. The first one has a "chair-like" configuration of the atoms and the second one exhibits a "layered" structure. Smith et al.[7] have shown that only for the orthorhombic crystal the special

deformation of the lattice gives rise to FSDP. They concluded that a-As is related to the orthorhombic crystal.

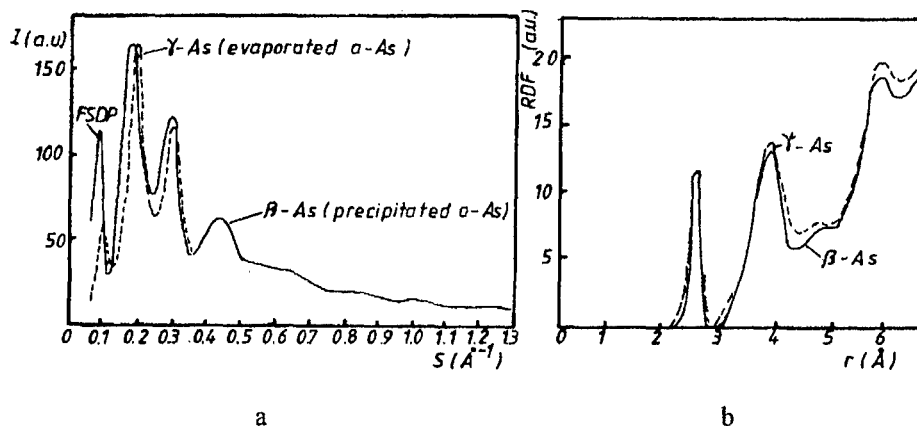


Fig. 1. The structure factor (a) and the radial distribution function (b) for the two forms of amorphous arsenic:  $\beta$  and  $\gamma$  arsenic.

Davis et al.[8] have built an amorphous arsenic (a-As) model with 533 atoms and computed its minimum free energy configuration. The authors concluded that the model reproduces quite well the experimental RDF. Nevertheless, two unresolved problems still remain: a). the explanation of the differences between  $\beta$ -As and  $\gamma$ -As in the frame of the CRN model and b). the aptitude of the model to reproduce FSDP. In order to explain the FSDP some authors assume the existence of definite molecular species in the material (e.g.  $\text{As}_4$  molecules found, also, in the vapour phase).

In modeling the structure of disordered three-fold coordinated arsenic we started from the assumption that disordered folded layers are the main constituents of the non-crystalline phases. This idea seems to have the chance to explain the increase of the internal distance deduced from the position of the FDSP,  $d$  FDSP, when one passes from crystal to amorphous phase. In the same time the way seems to be opened to explain the structural differences between  $\beta$ -As and  $\gamma$ -As: in  $\gamma$ -As the disordered layers are highly interconnected and kept together by occasional bonds which, during annealing break and a new equilibrium distance between layers is established. Thus, the new relaxed form  $\beta$ -As is obtained. The distance  $d$  FDSP is larger for the relaxed case, as observed.

With the aim to shed more light on the structure of a-As we carried out structural simulations using atomic scale models. The free energy of a hand built model as a disordered layer with 146 atoms was minimized by computer using a Monte Carlo procedure. Bond stretching,  $f_1$  and bond bending,  $f_2$  force constants with  $f_2/f_1=1$  were used. An equilibrium distance  $r_1=2.51$  Å and a bond angle  $\alpha=98^\circ$  were used.

The main characteristics of the disordered layer with minimum free energy are:

- number of 5,6,7,8 -fold rings are 22,16,11,3, respectively.

- r.m.s. of  $r_1$  is 0.11 Å and r.m.s. of  $\alpha$  is  $7.87^\circ$ .

Now we shall try to prove the validity of the hypothesis regarding the structure with disordered layers for a-As. An important experimental finding in a-As and other glasses with arsenic[9] is that, as a general feature, the distance corresponding to the angular position of FSDP is significantly higher than the interlayer distance in the parent crystals. For a-As the interlayer distance is 5.85 Å, appreciably exceeding that of 5.50 Å for the interlayer distance in orthorhombic arsenic. No reasonable explanation for this difference was given up to day. It is quite improbable that the Van der Waals equilibrium distances between layers in amorphous and crystalline materials would be essentially different. Nevertheless, if one supposes that the effective thickness of the layers are different in the amorphous and crystalline phase, the apparent increase of the interlayer distance can be understood.

In order to determine accurately the thickness of the simulated irregular layer we computed the statistics of the height of the individual As-pyramids. We have obtained the mean value of the heights: 1.63 Å. If one takes into account that the layer thickness in As crystal  $d=1.25$  Å, then the increase in the layer thickness (from c-As to a-As) is 0.38 Å. This increase of the layer thickness

correspond to the increase of the interlayer distance and is in excellent agreement with the best experimental value:  $d = 5.85 - 5.50 = 0.35 \text{ \AA}$ .

Thus, on the basis of the above calculation, we can furnish a sound argument for the origin of FSDP in a-As, but the problem is now to stack layers in order to obtain a correct three-dimensional structure.

Three identical layers, shifted along the Oz axis by  $5.85 \text{ \AA}$  give rise to a spatial model, which is unsatisfactory as concerning the details of the RDF. To avoid the exact periodicity of the layers which constitute the model, each of them was differently oriented (rotated by  $\pi/2$ , reflected in the XOY plane). The resulting RDFs (especially for the model with reflection) after correction for their finite size, is in quite good agreement with the experimental RDF for a-As (Fig. 2)

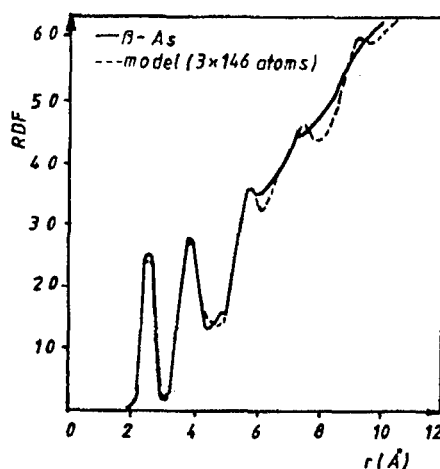


Fig. 2. The radial distribution function of the Popescu's model with disordered layers ( $3 \times 146$  atoms) compared to the experimental function.

The agreement of the experimental and model RDFs seems to be as good as the agreement of the experimental RDF and the RDF for the CRN model devised by Davis et al. A decisive test for the validity is however the aptitude of the model to reproduce the FSDP.

We performed a detailed analysis of several typical models for a-As: the Greaves-Elliott-Davis model [10], the Beeman's model (private communication of the coordinates) and our layered model (Popescu's model). Firstly, we calculated the structure factor in the region of the FSDP for the above models. Secondly, we calculated the hole radius distribution (in the models).

In order to determine the radius distribution of the holes in a given computer model we used a Monte-Carlo procedure. Starting from a given position inside the model, the distance  $d$  to the nearest atom was calculated. Afterwards, small random movements were given to this arbitrary position and were retained only those moves which led to higher radius of the hole. Finally the maximum radius was obtained. By repeating the procedure at different starting positions inside the model, the complete distribution of the holes was obtained.

While FSDP reflects the degree of layering of the model, hole radius distribution (HRD) accounts for the layer packing characteristics. Fig. 3 shows the structure factor in the FSDP range for various models of a-As and for crystalline As (c-As).

A significant correlation is evidenced between the height of the FSDP and the width of the HRD. If no layers are developed in the model, the FSDP is lacking (see the GED model). The Beeman's model exhibits a bimodal distribution of hole radii and this feature is correlated with the splitting of the FSDP. The Popescu's model with well-correlated layers shows a very strong FSDP. The peak developed by the crystal in the region of FSDP has low intensity. The r.m.s. of HRD in the GED model is large (not yet computed from the data given in Fig. 3 !) while for the Popescu's model is narrow. We must point out that the careful investigation of the Beeman's model (633 atoms) has evidenced some compressed regions with the tendency to raise the first coordination sphere and

regions with lower density (normal coordination sphere:  $N=3$ ). This inhomogeneity seems to be responsible for the split FSDP.

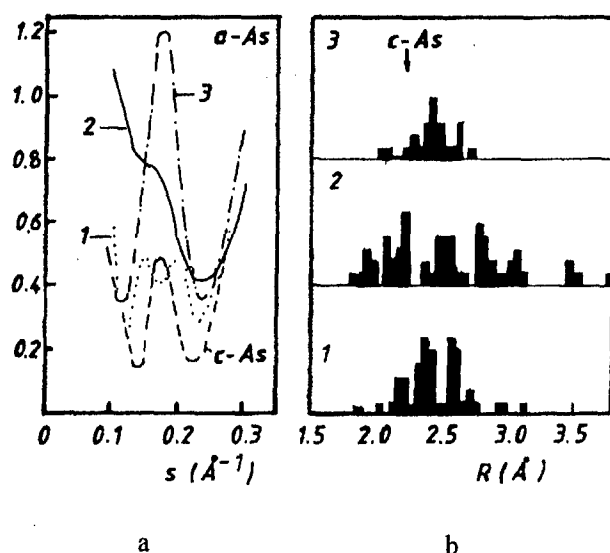


Fig. 3. The FSDP region (a) and the hole radius distribution (b) in three models for a-As: 1. Beeman's model; 2. GED's model; 3. Popescu's model.

As a conclusion it seems plausible to have layered configurations in amorphous arsenic.

One important result of this modelling is the discovery of the relation between the quasi-periodicity obtained from the position of the FSDP,  $d_{\text{FSDP}}$ , and the inter-layer distance, as introduced in the models. Fig. 4 shows the results.

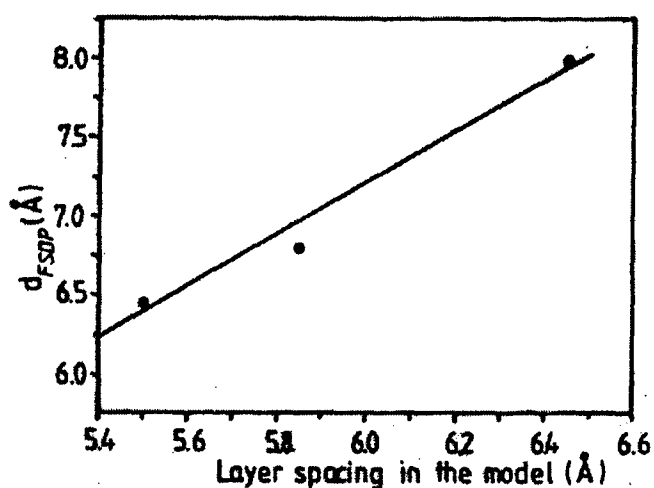


Fig. 4. The relation between the quasi-periodicity distance characteristic to FSDP position, calculated from arsenic models, and the inter-layer distance,  $d_{\text{model}}$ , in the same physical models.

The following correlation holds:

$$d_{\text{FSDP}} = 1.23 d_{\text{model}} \quad (1)$$

A simple explanation of this relation is related to the waved character of the disordered layers. The mean interlayer distance for a waved atomic configuration is, obviously, larger than that of a

"planar" configuration. Thus, the modelling results bring a firm proof for the waved layer structure of amorphous arsenic, which can be extended to other layered chalcogenide alloys.

It is remarkable that Apling et al. [11] found a relation between the quasi-periodicity,  $d_{\text{FSDP}}$ , calculated from the FSDP position in  $\text{As}_2\text{S}_3$  films, and the diameter,  $d_{\text{mol}}$ , of the molecular  $\text{As}_4\text{S}_6$  ( $\sim 6.5$  Å), as  $d_{\text{FSDP}} = 0.83 d_{\text{mol}}$ .

### 3.2. Amorphous $\text{As}_2\text{Se}_3$

The intensity patterns of the X-ray diffraction in binary chalcogenide glasses of composition  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ ,  $\text{As}_2\text{Te}_3$  and of their alloys show obvious similarities. The most striking one is the presence of the FSDP around  $s \sim 0.1$  Å<sup>-1</sup>.

The structure of some As-Se glasses was modelled by Rehtin and Averbach [12]. In the framework of their computer model, the free energy minimization was avoided: a quasi-random assembly of As and Se atoms was arranged using a Monte-Carlo method so as to obtain a best fit to the radial distribution function (RDF) of the glass. For a- $\text{As}_2\text{Se}_3$  the authors claim a very good agreement of the experimental and model RDFs. Nevertheless, if one computes the structure factor  $I(s)$  of the model, a discrepancy does appear in the region of the FSDP. The  $I(s)$  curve calculated by us on the basis of published data in [13] does not exhibit any FSDP.

A continuous random model (CRN) for a- $\text{As}_2\text{Se}_3$  (a cluster with 146 simulated atoms) of minimum free energy was devised by Prof. Grigorovici and me. Although the RDF of our model seemed to be quite satisfactory (Fig. 5b), the calculated  $s.I(s)$  again did not reproduce the FSDP (Fig. 5a). We are forced to conclude that a true random model for this glass is inadequate.

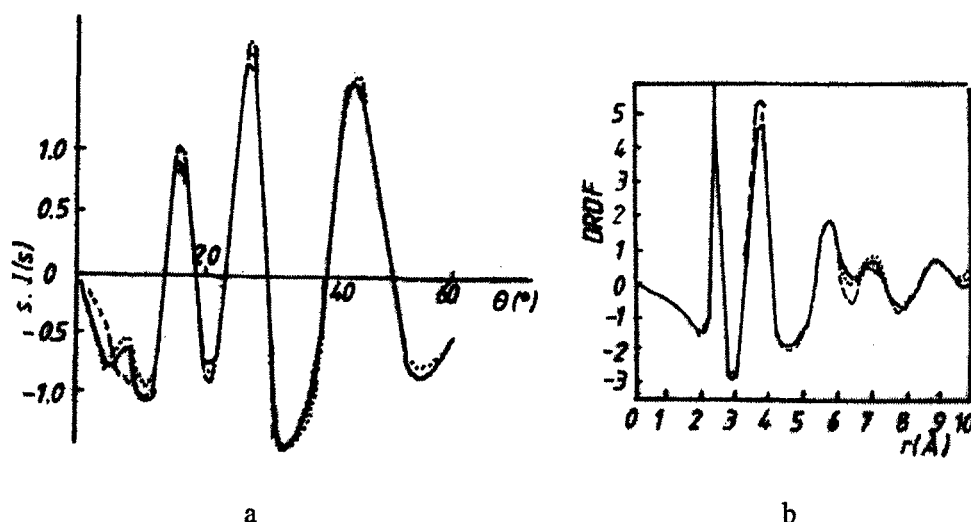


Fig. 5. Modelling results for  $\text{As}_2\text{Se}_3$ . (--- CRN model; — LCRN model; — experiment).

A new model with 146 atoms, with a bias towards a layered structure (LCRN) was obtained by changing the bonding pattern in the initial CRN model of a- $\text{As}_2\text{Se}_3$ . Its atoms were partitioned into three superposed layers. Bonds were established chiefly among the atoms of each layer. Only four selenium atoms formed bridges between layers, two for each pair. The RDF of this layer-biased model differs only slightly from that of the CRN model, but its reduced structure factor  $s.I(s)$  displays the previously lacking FSDP (Fig. 5). This is a strong argument in favour of the structure with anisotropic, layer-like configurations in arsenic chalcogenides.

### 3.3. Amorphous $\text{As}_2\text{S}_3\text{Ge}_x$

In the series of ternary chalcogenides, based on  $\text{As}_2\text{S}_3$  and allied with various content of germanium, the main feature in the structure factor is the appearance of a well-developed FSDP. Fig. 6 shows the X-ray diffraction pattern for several compositions in the system.

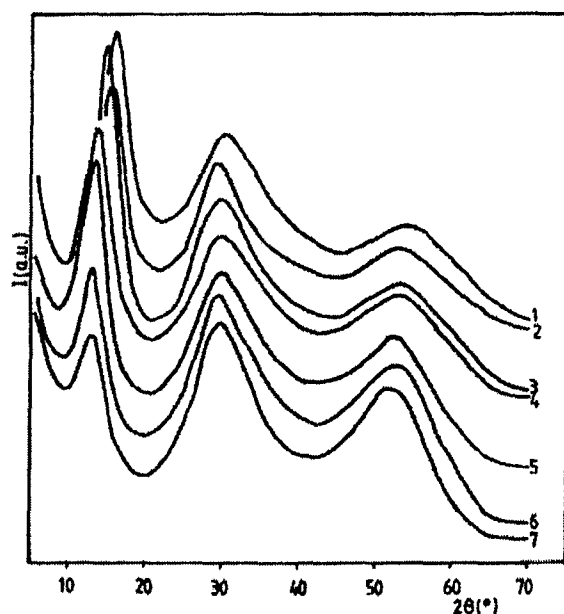


Fig. 6. X-ray diffraction pattern of  $\text{As}_2\text{S}_3\text{Ge}_x$  ( $x = 0.26; 0.68; 0.88; 1.67; 2.14; 2.70; 3.33$ ). Cu  $K_\alpha$  radiation. 1)  $x = 0.26$ ; 2)  $x = 0.68$ ; 3)  $x = 0.88$ ; 4)  $x = 1.67$ ; 5)  $x = 2.14$ ; 6)  $x = 2.70$ ; 7)  $x = 3.33$ .

Firstly, we must observe that the intensity of the FSDP firstly increases with  $x$  and, after reaching a maximum intensity around the composition  $x = 0.88$  decreases and becomes broader. A gradual shift of the FSDP position towards larger quasi-periodicity, when more and more germanium is added, is supposed to be correlated to the layer configurations in the material. We have used the detailed structural unit distribution deduced by Andreichin, Grigorovici et al. [14], for every composition  $x$  and have calculated the average thickness of the layers (it was assumed that the layer thickness is given by the mean value of the height of different structural units weighted by the compositional coefficients). We found the theoretical values of the interlayer distance,  $d_{\text{model}}$ . A comparison with the experimental values is shown in Fig. 7.

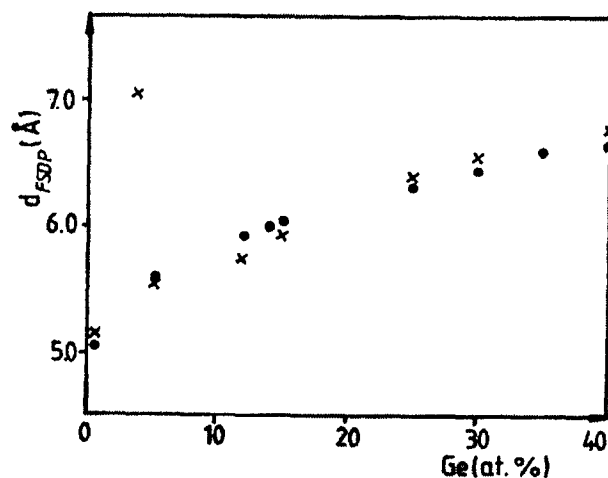


Fig. 7. The quasi-periodicity,  $d_{\text{FSDP}}$ , in the  $\text{As}_2\text{S}_3\text{Ge}_x$  system, as a function of the germanium content,  $x$ . (x – experimental points; • - theoretical, based on structural units).

The excellent agreement is a new argument in favour of the anisotropic configurations in glass. On the other hand we must stress that the strong intensity developed around the topological threshold  $Z = 2.67$  seems to indicate a maximum extension and alignment of the anisotropic configurations in this system.

### 3.4. The anisotropic configurations and the photo-anisotropy effect

The mechanism of the photoinduced anisotropy in chalcogenide glasses is still speculative. Nevertheless, several models have been developed. Grigorovici et al. [15] proposed the first model for the vectorial (anisotropic) reversible transformations in two stages, based on biphotonic processes, where VAP dipolar state is the same with that in the case of the scalar (isotropic) transformations, i.e. of the photodarkening (PD). The vectorial and scalar transformations differ only by the second stage of the induced modifications. In the scalar processes the polymerization has not a directional character. The two types of processes are necessarily limited to the materials where are possible the light induced transitions towards a metastable excited state with a different degree of structural connectivity. In the vectorial transformations, the second stage leads to a preferential orientation of the covalent bonds due to the directional character of the interaction between the VAP dipole and the electric field of the incident light wave.

Lyubin and Klebanov [16] discussed the various possible mechanisms for the photoanisotropic transformations and concluded that the mechanisms are different for the cases of excitation in different spectral ranges. At the sub-band-gap excitation, light creates scattering centers in the glass. Such centers will scatter the light isotropically, anisotropically or gyrotropically depending on the polarization state of the inducing radiation. In the case of the super-band-gap light, the excited radiation is able to orient and reorient the main interatomic covalent bonds of the glass.

In the framework of our models with anisotropic disordered configurations of atoms, it is possible to explain the anisotropy induced by polarized light. The system of anisotropic, layer-like configurations, looks are an assembly of domains which can be partially oriented by elementary bond breaking and rebonding processes, which fact induces a macro-anisotropy observed in many cases. An example case of bond switching can be followed in Fig. 8.

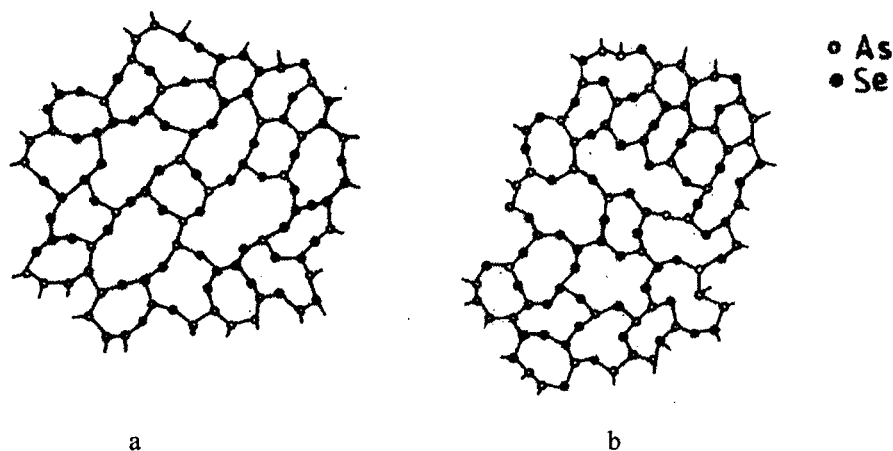


Fig. 8. The relaxed layer configuration in  $\text{As}_3\text{Se}_2$  (a) and the stressed configuration (b) obtained by bond switching within the atomic configuration.

If one supposes that a quantum of polarized light is acting on the configuration, then the orbitals situated in the direction of oscillation of the electrical vector, that takes part into the covalent bond, are excited, the bond breaks and the energy in excess allows for a new bonding within the configuration. This effect is facilitated for the atoms with more distorted bonds. In our case when two bonds are broken by a two photon process, then new bonds can be formed, and, as a consequence, other two breaking are committed in order to compete with the loss of distortion energy. A new metastable configuration correlated with the orientation of the neighbouring configurations (this is somewhat similar to the case of cooperative orientation of the magnetic domains) account for new directional properties: photoinduced macro-anisotropy. Energetical relaxation of the models with 110 atoms (Fig. 8) shows that the difference between the free energy of the two configurations is enough low to account for a possible photo-induced effect when the material is illuminated by laser light, as observed in the experiment.



#### 4. Conclusions

The ball and stick modelling combined with the computer relaxation of the models provide important informations on the structure of non-crystalline chalcogenides. The anisotropic configurations of atoms demonstrated in the structure of arsenic based chalcogenides, proved to be useful in the explanation of the photoinduced anisotropy in glassy chalcogenides. The anisotropic domains switch their bonding according to the direction of the polarization vector of the exciting light and determine new bonding and orientation of the anisotropic cluster, within a cooperative effect shared by the neighbouring configurations, that gives rise to the macroscopic anisotropy observed in these materials.

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